OCH REGISTRERINGSVERKET Patentavdelningen

PCT/SE 0 3 / 0 1 4 9 2

REC'D 0 9 OCT 2003

WIPO PCT





Härmed intygas att bifogade kopior överensstämmer med de handlingar som ursprungligen ingivits till Patent- och registreringsverket i nedannämnda ansökan.

This is to certify that the annexed is a true copy of the documents as originally filed with the Patent- and Registration Office in connection with the following patent application.

- (71) Sökande Linde AG, Wiesbaden DE Applicant (s)
- 0202836-3 (21) Patentansökningsnummer Patent application number
- (86) Ingivningsdatum Date of filing

2002-09-25

Stockholm, 2003-09-30

För Patent- och registreringsverket For the Patent- and Registration Office

Sonia André

Avgift Fee

> PRIORITY DOCUMENT SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

METHOD AND APPARATUS FOR HEAT TREATMENT

FIELD OF INVENTION

The present invention relates generally to a method and an apparatus for heat treatment of materials, preferably metals, and more particularly to heat treatment involving low NOx emissions in open flame and radiant tubes as well as a very high thermal efficiency using radiant tubes.

10 BACKGROUND

20

Conventional oxy-fuel technology has successfully been used for many years. It provides great benefits regarding productivity and fuel consumption. Conventional oxy-fuel technology can also be used to achieve considerable reductions in Nox emissions compared to conventional air-fuel burner technology. However, oxy-fuel technology is relatively sensitive to air in-leakage into the combustion zone and requires good pressure control in the furnace. In some processes and furnace types it is very difficult to keep air from leaking into the system

Thus, fuel combustion in a furnace can result in large emissions of nitrous oxides (NOx). NOx (mainly NO₂) emissions have been found to have negative health effects, promote corrosion, and to be an environmental hazard, contributing among other things to eutrophication.

Large quantities of nitrous oxides are emitted to the ambient air when treating products in a furnace using conventional and even modern air-fuel burner technology.

30 In burner arrangements comprising radiant tubes, NOx

contents of 200-250 mg/MJ are not uncommon, being far above the limits set by authorities to reduce the environment damaging emissions.

A further problem when using a conventional oxy-fuel burner for heat treatment of metals using radiant tubes is that the high flame temperature of an oxy-fuel burner will damage the tube material, which of course is unacceptable.

SUMMARY OF THE INVENTION

10 An object of the present invention is to provide a method and an apparatus for heat treatment of metals wherein the drawbacks of prior art apparatuses are eliminated or at least mitigated. A particular object is to provide a method and an apparatus wherein emission of nitrous oxides (NOx) is kept to a minimum while maintaining a high degree of thermal efficiency and providing technology to use oxy-fuel combustion in radiant tubes.

The invention is based on the realization that an oxyfuel burner can be used for low NOx, high efficiency
heat treatment of metals by providing for a recirculation of hot gas exhausts resulting from an ejector
effect provided by the oxygen nozzles of the burner.

According to the invention there is provided a method of heat treatment of materials as defined in claim 1. There is also provided an apparatus for heat treatment of materials as defined in claim 8.

With the inventive method and apparatus the abovementioned drawbacks of prior art are eliminated or at least mitigated. The method provides for an environmentally friendly and at the same time cost effective process.

- In a particularly preferred embodiment, the invention is used in combination with radiant tubes, allowing the invention to be used in protective atmosphere processes. These atmospheres are normally all atmospheres other than the atmosphere resulting form combustion of hydrocarbons.
- 10 Further preferred features are defined in the dependent claims.

BRIEF DESCRIPTION OF DRAWINGS

The invention is now described, by way of example, with reference to the accompanying drawings, in which:

- 15 Fig. 1 shows a longitudinal elevation sectional view through an apparatus according to the invention;
 - Fig. 2 is a transverse cross sectional view from line II-II of Fig. 1;
- Fig. 3 is an overall sectional view of a burner and 20 radiant tube arrangement;
 - Fig. 4 is a diagram showing typical temperature profiles for different types of combustion;
- Fig. 5 is a diagram showing flame and recirculation temperatures during operation of an apparatus according to the invention; and

Fig. 6 is a diagram showing resulting equilibrium NO concentrations as well as two measured results.

DETAILED DESCRIPTION OF THE INVENTION

In the following a detailed description of preferred

5 embodiments of the present invention will be given. In
Fig. 1 there is shown a sectional view of a burner
arrangement, generally designated 1. The burner arrangement comprises an insert 10 having a generally circular
cross-section, see fig. 2. The insert is arranged to be

10 mounted through a hole in a wall 12 of a furnace (not
shown), as is conventional. It is also preferred to
arrange a heat insulating material 14 on the hot side of
the burner mounting plate 12.

In the burner body, a fuel supply pipe 16 is centrally provided for supplying fuel, such as natural gas, to a burner reaction zone or flame 26, a portion of which is shown in figure 1. The fuel supply pipe is in one end provided with a connector arranged to be connected to a source of fuel (not shown) and in the other end with a fuel nozzle 16a.

Oxygen is supplied through six equidistant pipes 18 placed at a constant distance from the centre axis of the insert 10, see fig. 2. The oxygen supply pipes are in one end provided with a respective connector arranged to be connected to a source of oxygen (not shown) and in the other end with a respective oxygen nozzle 18a having a cross-sectional area of A3. The oxygen nozzles are streamlined, thus minimizing turbulence of the oxygen leaving the nozzle, preferably at supersonic velocities.

30 The effect of this will be explained further below.

An annular exhaust opening 20 is provided outside of the oxygen pipes 18. This opening is provided for accommodating recirculation of exhausts resulting from the heating process involving the burner. The exhaust opening is separated from the oxygen pipes by a comparatively thin wall, thereby providing for a heat exchange between the hot exhausts from the burner process and the relatively cold oxygen supplied through the oxygen pipes 18. This heat exchange provides for a high thermal efficiency, in all cases above 90%, resulting in a very energy efficient process, with low exhaust gas temperatures.

10

15

20

30

Finally, there is provided a circular flame tube 22 at the front end portion of the insert, having a crosssectional area A2 and a diameter L2. The flame tube surrounds the fuel and oxygen nozzles 16a, 18a and extends a distance L1 from the oxygen nozzles. The primary function of the flame tube is to form a mixing compartment for oxygen and recirculated exhaust gas in a first mixing step and to direct the resulting jet momentum forwards. Six equidistant apertures 24, each having an area Al, are provided in the flame tube - each one outside of a respective oxygen nozzle 18a. In that way, an ejector function is obtained whereby exhausts from outside of the flame tube 22 is sucked into the 25 same. The implication of that will be explained in the following in connection with the description of the method according to the invention.

In order to start the burner, fuel and oxygen are supplied from a respective source to the respective pipes. The fuel can be any gaseous fuel, such as,

natural gas, propane, coke oven gas, etc having a combustible content, or any liquid fuel, such as light to heavy fuel oil, emulsions containing carboneous substances, etc.. By oxygen is in this context meant a gas with an O2 content exceeding 21% by volume, and preferably exceeding 30%, more preferably above 40%, even more preferably more than 70%, in a preferred embodiment more than 85%, such as in standard gas commercially available on the market, but essentially pure oxygen, containing 99.5% oxygen or more, can also be used.

Besides oxygen, the oxidizing gas comprises other elements usually found in air, such as nitrogen and argon. To ignite the flame, a pilot burner (not shown) is provided in the insert 20.

and the fuel maintains the reaction zone 26 so as to provide a heating source. The operation of the oxy-fuel burner 20 is controlled by means of the amount of fuel and oxygen supplied at high velocities through the fuel 20 and oxygen pipes, respectively. The oxy-fuel mixture results in the reaction zone 26 having properties, such as length, temperature etc., that are controlled by the supply rate of fuel and oxygen. The higher the oxygen content is in the reaction zone, the higher the flame temperature will be, resulting in a theoretical flame temperature of 1200-2700°C.

In the flame, the oxygen and the fuel react according to the following formula:

$$xCyE + (x + y/4)O_2 => xCO_2 + y/2H_2O + Energy$$
 (1)

30 wherein x is molefraction of Carbon (C) in fuel, and

y is molefraction of Hydrogen (H) in fuel.

In addition to this the recirculated exhaust gas is influencing the flame temperature as described in the following formula

5 a*Fuel+b*Oxygen+c*Exhaust_{Trecirc}=>(a+b)*Prod+c*Exhaust_{Tflue}(2)
wherein

 T_{recirc} = temperature of exhaust when recirculated,

 T_{flame} = temperature of exhaust after reaktion (1)and(2),

Tflame > Trecirc,

10 a = mass flow of fuel, b = mass flow of oxygen, and
c = mass flow of recirculated exhaust.

The recirculation factor, c/b, is typically above 10.

The exhausts created in the process can contain among other things nitrogen, which, together with oxygen,

15 forms unwanted NOx gases, mainly NO, which in nature is transformed into NO2.

The formation of thermal NO is described by the Zeldovich mechanism according to the following formula:

$$O + N_2 = NO + N$$
 $k = 6.89E13 * exp(-75100/R/T)$

20 N + O_2 = NO + O k = 9.81E9 * exp(-6610/R/T)

$$N + OH = NO + H$$
 $k = 4.20E13$

Resulting equilibrium NO concentrations as a function of PO_2 , PN_2 and Temperature can be seen in Fig. 6.

As mentioned above, the oxygen is supplied at high velocities, preferably at supersonic velocities. These velocities, together with the configuration of the apertures 24 in the flame tube and the shape of the oxygen nozzles 18a and positions thereof relatively to the respective hole, create an ejector effect sucking the flame exhausts into the flame tube, as indicated by arrows in fig. 1. In a preferred embodiment, the oxygen nozzles are Laval shaped and aerodynamic.

10 After having been sucked into the flame tube 22, a minor portion of the recirculated exhausts leaves the burner arrangement through the exhaust pipe 20. In the exhaust pipe, the hot exhausts leave part of their heat energy to the oxygen being supplied to the burner in the oxygen pipes 18 in a heat exchange process. This heat exchange process contributes to the high efficiency of the burner arrangement and process according to the invention.

20

However, a major part of the exhausts are recirculated to the burner process by mixing thereof with the oxygen leaving the oxygen nozzles 18a, forming the primary recirculation mixture. Prior to being ignited, the oxygen containing mixture resulting from the primary recirculation is further mixed with the fuel and more exhaust gas in a second recirculation step. This mixture is thus ignited and forms an extended reaction zone. It is thus realised, that the combination of among other things the parameters Al, A2, A3, L1, and L2 is of vital importance to effect the proper mixing of oxygen and exhausts. In a preferred embodiment, the following combination is provided: A1>>A3, A2 ≤ EA1 (area of all apertures 24), and/or L1 ≥ L2.

As already stated, the higher oxygen content, the higher temperature. The high theoretical flame temperatures obtained with oxy-fuel burners could be disadvantageous in certain heat treatment processes wherein the material to be heated must be brought to very uniform temperatures. By lowering the oxygen content of the oxygen containing gas supplied to the burner, the flame temperature is lowered to desired temperatures while the high NOx promoting temperatures are avoided, see Fig. 4.

10 As mentioned above, a secondary recirculation of exhausts is also provided just down-stream of the flame tube 22, as indicated by the arrows in fig. 1. This additional dilution of the oxygen content further helps to lower the temperatures of the flame. This gives so-called flameless combustion, which is accomplished by the high velocity fuel injection in combination with a streamlined fuel nozzle. As can be seen in fig. 1, the visible portion of the reaction zone 26 starts at a distance from the fuel nozzle, allowing for the recirculation of the exhausts prior to ignition. The effect of the recirculation factor, as defined above, and of the temperature of the recirculated exhaust gases on the resulting flame temperature can be seen in Fig. 5.

A second preferred embodiment of a burner arrangement according to the invention will now be described with reference to fig. 3, wherein a burner and radiant tube arrangement is shown. Thus, like in the first embodiment, a burner insert 10 is provided in an aperture in a furnace wall 12.

A radiant tube, generally designated 30, is provided in front of the burner insert 10 and having a diameter exceeding that of the flame tube 22. The use of a radiant tube is known per se and the radiant tube 30 com-5 prises an outer cylindrical tube 32 having a first open end facing the furnace wall 12 and a second closed end opposite of the first end. In the outer tube 32 there is provided an inner tube 34 having a diameter less than the inner diameter of the outer tube 32 so as to create an inner, essentially circular channel 36 and an outer, annular channel 38. The inner tube is kept in position in any suitable way, such as by means of flanges (not shown) extending outwardly there from. Also, the inner tube 34 is positioned with its first end ending a distance L3 from the front end of the flame tube 22 of the 15 burner and with its second end ending spaced apart from the closed end wall of the outer tube 32, thereby providing a recirculation path for exhausts.

10

In operation, the reaction takes place in the inner channel 36. Exhausts created in the combustion process 20 are guided through the inner channel, turn at the closed end of the outer cylinder 32, and return in the opposite direction through the outer annular channel 38. Thus, the radiant tube forms an essentially closed system.

The exhausts returning to the burner 10 are guided 25 either through the openings 24 in the flame tube, forming a primary recirculation path, or through the gap formed between the flame tube 22 and the inner tube 34, forming a secondary recirculation path. The proportion of exhausts of the first and secondary recirculation 30 paths is determined e.g., by the parameters A1, A2, L1, L2, and L3 as well as by the velocity of the oxygen and the fuel.

Method. Firstly, the burner arrangement according to the invention allows very high degree of recirculation of exhausts. This in turn allows for extremely low NOx emissions; figures showing as low as 0-25 mg/MJ NOx have been obtained during test runs, depending on the N2 content. An oxygen content below 15% in the reaction zone has been found feasible. Secondly, and particularly in the second embodiment, a very high thermal efficiency is obtained, resulting in a cost-effective process.

Preferred embodiments of a method and an apparatus for heat-treatment of materials according to the invention have been described. A person skilled in the art realizes that these could be varied within the scope of the appended claims. Thus, although a preferred burner configuration having six oxygen nozzles has been shown, this configuration can be varied so that e.g. four nozzles or any other number or oxygen nozzles are provided.

CLAIMS

- A method of heat-treatment of materials, prefer ably metals, said method comprising the following steps:
 - providing and maintaining a flame by supplying a burner with fuel and gas containing at least 30 percent by volume oxygen;
- creating an oxygen-exhaust mixture by recirculating
 exhausts from said flame to said gas containing at
 least 30 percent by volume oxygen by means of an
 ejector effect;
 - mixing said oxygen-exhaust mixture and said fuel; and
- providing a secondary recirculation by recirculating
 exhausts from said flame to said oxygen-exhaust-fuel
 mixture.
 - 2. The method according to claim 1, wherein the step of recirculating exhausts comprises recirculating hot exhausts.
- 20 3. The method according to any of claims 1-2, wherein the step of supplying a gas containing oxygen includes supplying a gas containing oxygen at supersonic velocities.
- The method according to any of claims 1-3,
 comprising the additional step of effecting a heat exchange between exhausts leaving the process and the oxygen supplied to the burner.
 - 5. The method according to any of claims 1-4, wherein the gas containing oxygen contains above 40%,

more preferably more than 70%, even more preferably more than 85%, and most preferably more than 99.5% by volume oxygen.

- The method according to any of claims 1-5, wherein the heat treatment includes heat treatment of steel.
 - 7. An apparatus for heat-treatment of materials, preferably metals, comprising:
- at least one fuel nozzle (16a) connectable to a fuel source;
 - at least one gas nozzle (18a) connectable to a source of gas containing at least 30 percent by volume oxygen;
- wherein said at least one fuel nozzle and said at
 least one gas nozzle are arranged so at so provide a reaction zone (26);

characterized by

- means (24) for supplying exhausts from said flame to gas leaving said at least one gas nozzle by means of
 an ejector effect, and
 - wherein said at least one fuel nozzle (16a) is provided downstream of said at least one gas nozzle (18a).
- 8. The apparatus according to claim 7, comprising a flame tube (22) arranged around said gas nozzles, wherein the flame tube is provided with openings (24)

arranged outside of a respective of said at least one gas nozzle (18a).

- 9. The apparatus according to claim 7 or 8, wherein said at least one fuel nozzle (16a) is centrally provided in the apparatus.
- 10. The apparatus according to any of claims 7-9, wherein said at least one gas nozzle comprises at least two, more preferably four or six equidistant nozzles (18a) provided at a constant distance from a centre axis of the apparatus.
- 11. The apparatus according to any of claims 7-10, wherein said at least one gas nozzle (18a) is Laval shaped and/or aerodynamic.
- 12. The apparatus according to any of claims 7-11,
 wherein said at least one fuel nozzle (16a) is
 streamlined so as to allow for flameless combustion.

10

- 13. The apparatus according to any of claims 7-12, comprising an essentially annular exhaust opening (20).
- 14. The apparatus according to claim 13, wherein
 20 the essentially annular exhaust opening (20) is arranged
 to provide for a heat exchange with the gas supplied to
 said at least one gas nozzle.
- 15. The apparatus according to any of claims 7-14, comprising a tube (22) provided in front of the gas and fuel nozzles (16a, 18a), wherein the tube (30) comprises an outer cylindrical tube (32) having a first open end facing the gas and fuel nozzles and a second closed end opposite of the first end, and an inner tube (34)

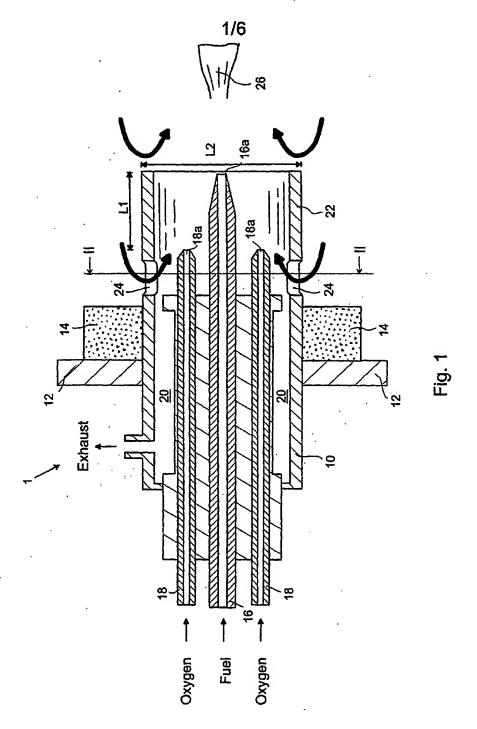
provided in the outer tube (32) and having a diameter less than the inner diameter of the outer tube (32) so as to create an inner, essentially circular channel (36) and an outer, annular channel (38).

5 16. The apparatus according to claim 15, wherein the inner tube is positioned with its first end ending a distance (L3) from a front end of the flame tube (22) and with its second end ending spaced apart from the closed end wall of the outer tube (32), thereby providing a secondary recirculation path for exhausts.

ABSTRACT

A method and an apparatus for heat-treatment of materials, preferably metals, are provided. The method comprises the following steps: providing and maintaining a
flame by supplying a burner with fuel and gas containing
at least 30 percent by volume oxygen; creating an
oxygen-exhaust mixture by recirculating exhausts from
said flame to said gas containing at least 30 percent by
volume oxygen by means of an ejector effect; mixing said
oxygen-exhaust mixture and said fuel; and providing a
secondary recirculation by recirculating exhausts from
said flame to said oxygen-exhaust-fuel mixture. The
method and apparatus allow for extremely low NOx
emissions and high efficiency, resulting in a an
environmentally friendly and at the same time cost
effective process

20 (Fig. 1)



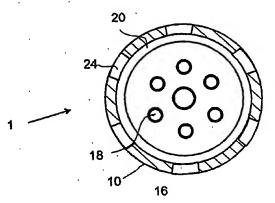


Fig. 2

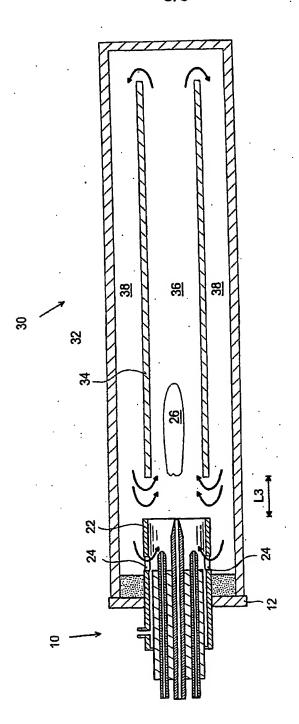


Fig. 3

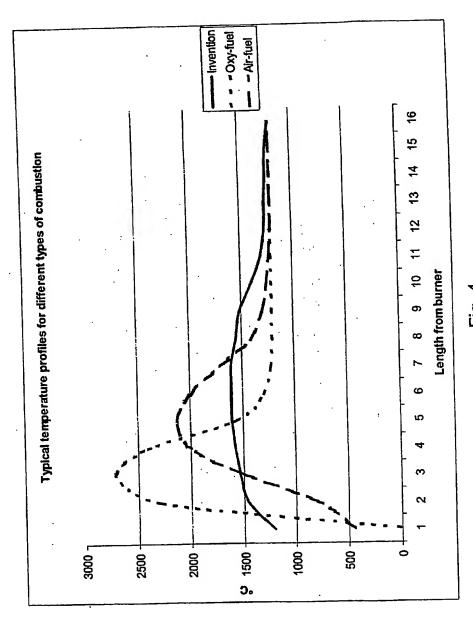


Fig. 4

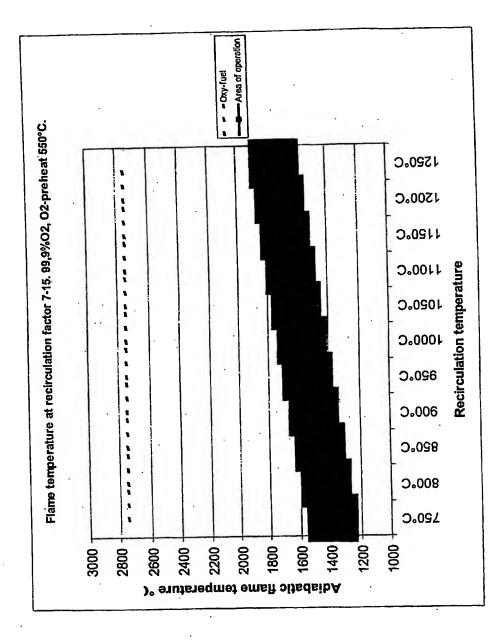
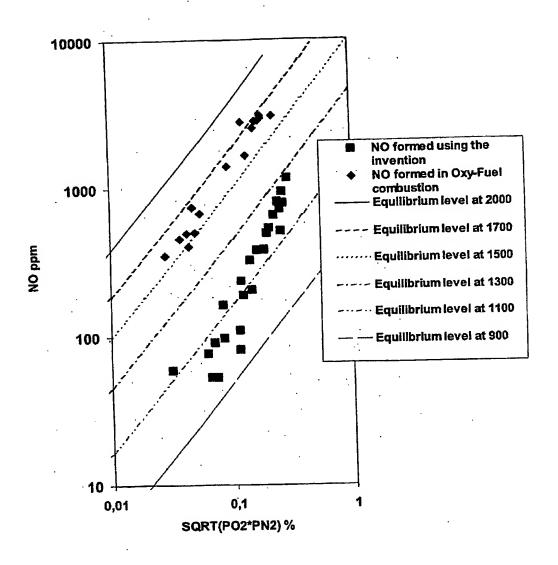


Fig. 5



This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

□ BLACK BORDERS
 □ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
 □ FADED TEXT OR DRAWING
 □ BLURRED OR ILLEGIBLE TEXT OR DRAWING
 □ SKEWED/SLANTED IMAGES
 □ COLOR OR BLACK AND WHITE PHOTOGRAPHS
 □ GRAY SCALE DOCUMENTS
 □ LINES OR MARKS ON ORIGINAL DOCUMENT
 □ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

IMAGES ARE BEST AVAILABLE COPY.

☐ OTHER:

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.